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AB INITIO STUDY OF REACTION MECHANISM OF OZONE WITH ETHENE AND ITS MONOHALOGENATED DERIVATIVES

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The reactions with ozone, beside the reactions with hydroxyl and nitrate radicals, represent the most important tropospheric sink for biogenic and anthropogenic alkenes. For that reason, in the past 40 years a number of studies have dealt with their kinetic and mechanistic aspects. Although the overall kinetics of these reactions is largely known nowadays, there is still a considerable uncertainty regarding their detailed mechanisms and product yields. In this work ab initio CASSCF and CASPT2 methods were employed in studying the reaction mechanisms of ozone with ethene, fluoro- and chloroethene up to the formation of the primary addition product (ozonide). Structural and electronic properties of the reactants, transition states and addition products were determined and discussed. Also given are the analyses of kinetic parametres in terms of the simple transition state theory (TST). Finally, in case of the ozone addition to ethene, reaction path study (IRC) was carried out and led to the determination of an approximate structure of the pre-reaction van der Waals complex. Whenever possible, a comparison is made between the theoretical and experimental values and these are generally in a good agreement.